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ABSTRACT:

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(54) IMPROVEMENTS IN OR RELATING TO METHANOL SYNTHESIS CATALYSTS

- (71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a process for the manufacture of methanol by reacting a gas mixture containing carbon monoxide, carbon dioxide and hydrogen in the presence of a catalyst containing zinc, copper and aluminum.
- 15 It also relates to a method of manufacturing the catalyst.
- It is known that mixtures of carbon monoxide and hydrogen, optionally containing carbon dioxide, may be converted to methanol in the presence of catalysts at pressures between 30 and 400 atm. and temperatures between 200° and 400°C (cf. Emmett in "Catalysis" Vol. III, pp. 351 et seq.; J. Schmidt, "Das Kohlenmonoxid", 2nd Edition 1950, pp. 189—220; "Ullmanns Encyklopädie der technischen Chemie", Vol. 12, pp. 403 et seq.).
- 20 The catalysts used are primarily zinc oxide/chromium oxide catalysts or copper catalysts and they may additionally contain other oxides as promoters. The numerous known processes for the synthesis of methanol do not satisfy all requirements as regards economy of operation and the activity and life of the catalysts used in commercial processes.
- 30 German Printed Application DAS 1,241,429 describes a process in which catalysts based on Cu/Zn/Cr oxides are used for the synthesis of methanol, copper contents of the order of 65—70% of the total metal content being used to achieve high catalytic activity.

According to German Printed Application DOS 1,568,864, methanol synthesis can be carried out in the presence of catalysts which contain the oxides of copper and zinc and at least one difficultly reducible oxide of a metal in Groups II to IV of the Periodic Table. The preferred difficultly reducible metal oxide used is aluminum oxide or magnesium oxide. To achieve a high catalyst activity in this system, it is also necessary to use a catalyst with a high copper content of preferably more than 35%, by metal atoms. The catalyst is produced from the components by precipitating the nitrates together by means of a soda solution or bicarbonate solution to give a mixture of carbonates and hydroxides when the pH is adjusted to values in the range of pH 7±0.5. Precipitation must also be carried out as quantitatively as possible. By drying at 105—150°C followed by calcining at from 200° to 300°C, the precipitate is converted to the oxide mixture, which is compressed and used in the synthesis. Due to their high copper content and mode of manufacture, the catalysts thus obtained show poor thermal stability and recrystallize very readily, so that their life is very restricted at high gas throughputs and pressures of more than 100 atm. A similar methanol synthesis is described and claimed in U.K. Specification No. 1,159,095.

45 However, we have found that in the above catalyst system copper/zinc/aluminum oxide, catalysts of substantially greater activity and longer life may be obtained if a compound belonging to a certain mixed crystal series is precipitated under specific conditions from an aqueous solution containing the components Cu, Zn and Al.

50 The present invention provides a method of producing a catalyst for the manufacture of methanol by reaction of a gas mixture containing carbon monoxide, carbon dioxide and hydrogen at an elevated temperature and

pressure, which method includes the step of precipitating a compound of the mixed crystal series $(Cu_xZn_y)Al_2(OH)_{16} \cdot CO_3 \cdot 4H_2O$ (where x and y are numbers from 0.5 to 5.5 such that the sum of x and y is 6), at a pH in the range from 4.5 to 5.5 with an alkali metal carbonate, alkali metal bicarbonate or mixture thereof from an aqueous solution containing salts of copper, zinc and aluminium in relative proportion sufficient to form said compound of said mixed crystal series, followed by calcination and reduction of the compound that is precipitated.

The invention also provides a process for the manufacture of methanol by reaction of a gas mixture containing carbon monoxide, carbon dioxide and hydrogen at a temperature in the range from 200—350°C and under a pressure in the range from 50—250 atm in the presence of a catalyst according to the invention.

The atomic ratio of the sum of the divalent metals copper and zinc to the trivalent aluminium in the compounds of the mixed crystal series is constant at 6:2. If the atomic ratio of 6:2 between the divalent and trivalent metals is not maintained, there are obtained mixtures of hydroxides, hydroxycarbonates and possibly even carbonates of the individual metals. Such mixtures are catalytically much less active than catalysts obtained from the aforementioned mixed crystal series.

A decisive factor in determining the activity of the catalysts is that the compounds defined by the above formula must be produced in a pure form. The quality of the precipitate can be rapidly and easily controlled by X-ray analysis, as the aforementioned compounds produce a characteristic X-ray diffraction diagram. Such control has the great advantage of making it possible to ascertain, immediately after precipitation, whether the desired catalyst will have the required activity or not.

Suitable precipitants are alkali metal carbonates and bicarbonates and of the bicarbonates those of sodium and potassium have given particularly good results. Mixtures of the said precipitants may also be used. The activity of the catalyst is dependent on the special conditions of precipitation, which must be effected in a pH range of from 4.5 to 5.5 and preferably of from 4.8 to 5.2. In this pH range the aforementioned mixed crystal series is produced in a pure form.

Copper, zinc and aluminium are in the form of salts, preferably their nitrates, dissolved together in water in such proportions that the desired composition of the catalyst is obtained and the stoichiometry of the above formula is obeyed. The metal salt solution desirably contains a total of 0.5 to 5g/Mol/litre and preferably from 1.0 to 2g Mol/litre

of metal ions. It is heated preferably to temperatures of from 50° to 100°C and more preferably from 70° to 100°C and then treated with an aqueous solution of a precipitant at a similar temperature. The precipitant is preferably used in a concentration of from 1 to 2 Mol per liter. The pH of the mixture during precipitation is controlled by means of a pH meter. The precipitate consisting of the desired compound is filtered off, washed with water and dried, suitably at temperatures ranging from 50° to 200°C and preferably from 100° to 150°C. Calcination is effected by heating the dried compound preferably for from 12 to 24 hours at temperatures ranging from 200° to 500°C. The calcined product is compressed to pellets and then reduced by heating for example in a mixture of nitrogen and hydrogen for from 5 to 100 hours preferably within from 10 to 25 hours at temperatures ranging from 150° to 350°C.

Since the particles of active component in the precipitated compound which belongs to a mixed crystal series have atomic dimensions, there is an optimum distribution of the components in the material before and after calcination and in the calcined and reduced catalyst. Due to this extremely fine stage of subdivision, catalysts having a substantially lower content of copper achieve better activities than prior art catalysts of higher copper contents. This may be readily seen from the comparative experiments detailed in the following Table 1 when compared with the experiments shown in Table 2. The experiments described in Table 1 clearly show that the catalysts prepared in the manner proposed by the invention have a much higher activity than prior art catalysts of similar composition in the pressure range tested, as may be seen from space-time yields. A great advantage of the catalysts of the invention is that the catalysts may be used for much longer periods, if desired at higher throughputs and higher pressures, without their activity being diminished by recrystallization. In Table 2, a prior art catalyst having a copper content of 42% (which is in the preferred range for copper in the process described in German Printed Application DOS 1,568,866) is compared for durability with a catalyst having a lower copper content (approx. 18%). These comparative experiments testify to the superiority of the catalysts produced by the invention. The catalysts of the invention permit the methanol synthesis to be carried out at pressures of more than 100 atm. and throughputs of from 20 to 60 m³ of gas mixture per liter of catalyst per hour (STP) and thus improve the economy of the process, particularly in large plants.

TABLE 1

| Catalyst prepared according to present invention | Atomic proportions based on total metal atoms | | | Throughput* | STY** at 150 atmospheres | | 200 | X-ray analysis after precipitation |
|--|---|------|------|-------------|--------------------------|-------|-------|--|
| | Zn % | Cu % | Al % | | 100 | 150 | | |
| Example 1 | 62.5 | 12.5 | 25 | 10 | 2.086 | 3.198 | 3.290 | $\text{Cu}_1\text{Zn}_3\text{Al}_3(\text{OH})_{18}$ $\text{CO}_3 \cdot 4\text{H}_2\text{O}$ |
| DOS 1,568,864 | | | | | | | | |
| Example 1 | 79.5 | 15.0 | 5.5 | 10 | 0.286 | 0.463 | 0.850 | Mixture of hydroxide carbonates, carbonates and hydroxides of the components Cu, Zn, Al. |

* expressed in m^3 per liter of catalyst per hour (STP)

** Space-time yield expressed in kg of methanol per liter of catalyst per hour.

TABLE 2

Space-time yields at 150 atm. after various on-stream times

| Catalyst prepared according to present invention | Atomic proportions based on total metal atoms | | | Throughput* | STY** | | | | | |
|--|---|-------|------|-------------|-------|-------|--------|--------|--------|--------|
| | Zn % | Cu % | Al % | | 20 hr | 50 hr | 100 hr | 150 hr | 200 hr | 600 hr |
| present invention | 56.25 | 18.75 | 25.0 | 30 | 3,360 | 3,295 | 3,210 | 3,180 | 3,165 | 2,900 |
| DOS 1,568,864 | 54.0 | 42.0 | 4.0 | 30 | 3,015 | 2,762 | 2,680 | 2,430 | 2,195 | 1,630 |
| | | | | | | | | | | 830 |

* expressed in m^3 per liter of catalyst per hour (STP)** Space-time yield expressed in kg of methanol per liter of catalyst per hour $\times 1,000$.

The synthesis of methanol using the catalysts of the invention is carried out at temperatures ranging from 200° to 350°C and pressures ranging from 50 to 250 atmospheres.

5 The feedstock may consist, for example, of a mixture of carbon monoxide, carbon dioxide and hydrogen in proportions of from 0.1 to 0.3 and preferably 0.1 to 0.2 moles of carbon monoxide and from 0.01 to 0.2 and preferably from 0.03 to 0.15 moles of carbon dioxide per mole of hydrogen. The gas mixture may also contain nitrogen in a concentration of up to about 5% by volume and steam in a concentration of from 0.01 to 0.07 moles per mole of hydrogen in order to establish water equilibrium.

The partial oxidation of crude oils gives a synthesis gas of approximately the following composition: 47% by volume of CO, 48% by volume of H₂ and about 5% by volume of CO₂. The desired carbon monoxide content may be obtained by partial conversion of this gas, whilst the H₂S and COS may be washed out to leave residues of less than 1 ppm. The resulting synthesis gas of CO, CO₂ and H₂, conveniently supplemented by about 2% v/v of steam, may then be reacted over the catalyst of the invention.

30 The following is a description of the manufacture, according to the invention, of compounds of the said mixed crystal series illustrating continuous precipitation with alkali metal bicarbonate or carbonate.

Following said general description of the

process, the process of the invention is described with reference to the following Examples.

Continuous precipitation with alkali metal carbonate or bicarbonate:

The metals Cu, Zn, and Al in the form of salts are dissolved together in water and the solution is heated to the desired precipitating temperature (see above). In a separate vessel, an alkali metal carbonate or bicarbonate solution having a concentration of from 1 to 2 moles per liter is also heated to the said temperature. Precipitation is carried out in a cascade of stirred vessels. The rate of feed of the metal salt solution and the carbonate solution is adjusted in each case so that a pH of from 4.5 to 5.5 and preferably from 4.8 to 5.2 is maintained in the first vessel of the cascade. Material overflowing from the first vessel is stirred further in the next vessel and its pH is adjusted to 5.0 by the further addition to carbonate solution if necessary. The material overflowing from the second vessel passes directly to a filter press and is subsequently dried, calcined and reduced in the manner described above. The conditions of precipitation given in this specification must be strictly maintained, as the desired mixed crystal series can only result when these instructions are followed exactly.

The compounds show a characteristic X-ray diffraction diagram having the following d values given only for the strongest reflexions:

| d value | 7.60 | 3.80 | 3.32 | 2.65 | 2.58 | 2.28 | 1.93 | 1.53 |
|-----------------------------------|------|------|------|------|------|------|------|------|
| intensity* (assessed visually) | v.s. | f.s. | m | m | s | m | m | s |
| d value | 1.50 | 1.50 | | | | | | |
| intensity* (assessed visually) | m | m | | | | | | |

*intensity assessed in the following grades:

v.s. =very strong

s. =strong

f.s. =fairly strong

m. =medium

70 Depending on the composition of the series of mixed crystals, the d values or intensities may deviate from the values given above.

Some representatives of the mixed crystal series are described in the following Examples 1 to 9, in which parts are by weight.

EXAMPLE 1.

(a) Preparation of catalyst.

For the precipitation of the compound $\text{Cu}_2\text{Zn}_4\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, the following two solutions are prepared:
 solution 1: 2.415 parts of copper (II) nitrate trihydrate,
 14.875 parts of zinc nitrate hexahydrate and
 7.502 parts of aluminium nitrate enneahydrate
 are dissolved together in 80 parts of water;
 solution 2: 15.420 parts of sodium bicarbonate are dissolved in 183.6 parts of water.
 The two solutions are separately heated to 80°C and then mixed together with stirring whilst maintaining a pH of from 4.8 to 5.2. The resulting precipitate is filtered off and washed. A sample thereof is tested by X-ray analysis. The washed precipitate is then dried for 20 hours at 110°C and calcined for 20 hours at 350°C . 2 parts of graphite are added and the whole is compressed to 3×3 mm pellets.

(b) Reaction.

1 liter of the catalyst precursor thus obtained is packed into a tubular reactor. The catalyst precursor is reduced at atmospheric pressure by a gas mixture consisting of 98% v/v of N_2 and 2% v/v of H_2 . The temperature is raised at intervals of 8 hours from 150° to 170° to 190° to a final temperature of 230°C . At 230°C the said gas mixture is replaced by synthesis gas of the following composition: 70.6% v/v of H_2 , 22.6% v/v of CO , 6.1% v/v of CO_2 and 0.7% v/v of CH_4 . The pressure of the synthesis gas may be varied between 50 and 250 atm. At a constant throughput of 10m^3 per liter of catalyst per hour, the synthesis gas is passed through the reactor at a temperature of 230°C and pressures of 100, 150 and 200 atm. The reaction mixture leaving the reactor is cooled to 20 – 25°C in a tubular cooler at the synthesis pressure. The crude methanol thus condensed is separated and continuously relaxed to atmospheric pressure. The space-time yields obtained are 2,086, 3,198 and 3,290 parts respectively of methanol per part by volume of catalyst per hour for the pressures 100, 150 and 200 atmospheres respectively.

EXAMPLES 2 to 5.

By effecting continuous precipitation in the manner described above, the compound $\text{Cu}_2\text{Zn}_4\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was prepared using the following solutions:

solution 1: mixture of the following nitrate solutions all having concentrations of 2 moles per liter and combined in the proportions given (parts by volume) to form a single solution:

2 parts of copper nitrate solution,
 4 parts of zinc nitrate solution and
 2 parts of aluminium nitrate solutions;

solution 2: sodium carbonate solution having a concentration of 2 moles per liter.

Solution 1 and solution 2 are separately heated to 80°C in two vessels. Precipitation is effected in a cascade of stirred vessels, in the first vessel of which distilled water heated at 80°C is placed before precipitation is commenced, an electrode being in contact with said water for the purpose of measuring the pH. Solution 1 and solution 2 are separately pumped to said first vessel, the two streams of liquids being combined near the stirrer axle. The rates of feed of the solutions are regulated so that a pH of 5.0 is maintained in the stirred vessel. The material overflowing from the first vessel is stirred further in the second vessel. The pH of the contents of the second vessel is kept under constant control by means of an electrode and is maintained at values below 5.5. The material overflowing from the second vessel passes directly to the filter press, where it is filtered and subsequently washed until no more nitrate can be detected in the filtrate. The precipitate is dried at 150°C and then calcined for 12 hours at 350°C , shaped into pellets, packed into a tubular reactor and reduced as explained under 1b) above. The reaction is carried out in a manner similar to that described in Example 1 at various pressures and various throughputs expressed in m^3 per liter of catalyst per hour (STP). The space-time yields STY given in parts per part by volume of catalyst per hour were determined at various pressures and throughputs. The results are given in the following Table.

TABLE 3

| Example | 2 | 3 | 4 | 5 |
|----------------|-------|-------|-------|-------|
| Throughput* | 10 | 20 | 34 | 43 |
| Pressure (atm) | 50 | 100 | 150 | 200 |
| STY** | 1,300 | 2,625 | 4,121 | 4,279 |

* expressed in m^3 per liter of catalyst per hour (STP)

** expressed in kg of methanol per liter of catalyst per hour.

EXAMPLES 6 to 9.

Another catalyst is prepared from the compound $\text{Cu}_x\text{Zn}_y\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$; the preparation of the aforesaid compound and its conversion to the catalyst of the invention as well as the use of the catalyst, being carried

out as described in Examples 1a and 1b. The synthesis results are given, as in Examples 2 to 5, as space-time yields determined at various pressures and throughputs in the following Table.

TABLE 4

| Example | 6 | 7 | 8 | 9 |
|----------------|-------|-------|-------|-------|
| Throughput* | 23 | 34 | 41 | 47 |
| Pressure (atm) | 100 | 150 | 200 | 250 |
| STY** | 2,530 | 3,850 | 4,180 | 4,420 |

* expressed in m^3 per liter of catalyst per hour (STP)

** expressed in kg of methanol per liter of catalyst per hour.

WHAT WE CLAIM IS:—

1. A method of producing a catalyst for the manufacture of methanol by reaction of a gas mixture containing carbon monoxide, carbon dioxide and hydrogen at an elevated temperature and pressure, which method includes the step of precipitating a compound of the mixed crystal series



- (where x and y are numbers from 0.5 to 5.5 such that the sum of x and y is 6), at a pH in the range from 4.5 to 5.5, with an alkali metal carbonate or bicarbonate or mixture thereof from an aqueous solution containing salts of copper, zinc and aluminium in relative proportions sufficient to form said compound of said mixed crystal series, followed by calcination and reduction of the precipitate.

2. A method as claimed in claim 1 wherein the precipitation is carried out at a pH in the range from 4.8 to 5.2.

3. A method as claimed in claim 1 or 2 wherein the metal salt solution contains a total of from 0.5 to 5 g Mol/litre of copper, zinc and aluminium ions.

4. A method as claimed in any of claims 1 to 3 wherein the metal salt solution is treated with the alkali metal carbonate or bicarbonate or mixture thereof at a temperature of from 50 to 100°C.

5. A method as claimed in any of claims

1 to 4 wherein, after precipitation, the precipitate is filtered off, washed with water, dried at a temperature of from 100 to 150°C, calcined at a temperature of from 200 to 500°C and reduced by heating to 150 to 350°C in a mixture of nitrogen and hydrogen.

6. A method as claimed in claim 1 and substantially as hereinbefore described.

7. A catalyst when produced by a method as claimed in any of claims 1 to 6.

8. A process for the manufacture of methanol which comprises reacting a gas mixture containing carbon monoxide, carbon dioxide and hydrogen at a temperature in the range from 200 to 350°C and under a pressure in the range from 50 to 250 atm in the presence of a catalyst as claimed in claim 7.

9. A process as claimed in claim 8 carried out at a pressure of at least 100 atm.

10. A process as claimed in claim 8 or 9 carried out with a throughput of from 20 to 60 m^3 of gas mixture/litre of catalyst/hour (STP).

11. A process as claimed in claim 8 and substantially as hereinbefore described.

12. Methanol when manufactured by a process as claimed in any of claims 8 to 11.

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